Modeling viscosity of concentrated and mixed-solvent electrolyte systems

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Abstract

A comprehensive model has been developed for calculating the viscosity of aqueous or mixed-solvent electrolyte systems ranging from dilute solutions to fused salts. The model incorporates a mixing rule for calculating the viscosity of solvent mixtures and a method for predicting the effect of finite electrolyte concentrations. The mixing rule represents the viscosity of multi-component solvent mixtures using molar volumes and viscosities of pure components together with binary parameters. With this mixing rule, the viscosity of ternary systems can be accurately predicted using parameters determined from only binary data. The effect of electrolyte concentration on viscosity is modeled by combining a long-range electrostatic term obtained from the Onsager–Fuoss theory, a contribution of individual ions, which is quantified by the Jones–Dole B coefficients, and a contribution of specific interactions between ions or neutral species. Formulations have been developed for the contributions of individual ions and species–species interactions to account for the effect of multiple solvents. In addition to solvent composition, the species–species interaction term is also a function of ionic strength. The model accurately reproduces the viscosity of systems such as salts in water, organic or mixed water-organic solvents and aqueous acids or bases up to the pure solute limit. The model has been coupled with thermodynamic equilibrium calculations to reproduce the effects of complexation or other ionic reactions on viscosity.
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1. Introduction

Viscosity of electrolyte solutions is of considerable interest due to its importance in numerous industrial systems, especially those involving electrochemical processes. Variations of viscosity with temperature and solvent composition have also been investigated to understand ion–solvent interactions in electrolyte systems. Extensive experimental viscosity data are available for both aqueous and mixed-solvent electrolyte systems. However, analysis of such data has been commonly performed only on a case-by-case basis and no attempt has been made to develop a comprehensive viscosity model for mixed-solvent electrolyte systems.

Theoretical investigations of viscosity of electrolyte solutions have been focused mainly on systems containing a single solute in dilute solutions with a single solvent, usually water. These theories resulted in the development of a limiting law, which predicts the relative viscosity of the solution as a function of the square root of the concentration in binary systems:

$$\frac{\eta}{\eta_0} = 1 + Ac^{1/2} \tag{1a}$$

The viscosity A coefficient was shown to be a function of solvent properties and limiting conductivities of ions. The limiting law was extended to somewhat higher concentrations (up to ca. 0.1–0.2 M) by Jones and Dole [1], who introduced the viscosity B coefficients, i.e.,

$$\frac{\eta}{\eta_0} = 1 + Ac^{1/2} + Bc \tag{1b}$$

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A further empirical extension of the Jones–Dole equation was proposed by Kaminsky [2], who introduced an additional quadratic term in *c*. The *B* coefficients in the Jones–Dole equation are characteristic for individual ions and can be interpreted in terms of ion–solvent interactions. Furthermore, they are additive in terms of contributions from individual cations and anions in a given solvent.

While accurate for relatively dilute solutions, the Jones–Dole equation and its simple extensions cannot reproduce experimental data for concentrated systems. Therefore, more comprehensive models have been recently developed for concentrated solutions. Jiang and Sandler [3] combined liquid-state and absolute-rate theories and developed a model that correlates viscosity data for 20 aqueous binary alkali halide solutions for concentrations up to $12\,mol\,dm^{-3}$ at $25\,°C$. Lencka et al. [4] developed a speciation-based viscosity model for concentrated multi-component aqueous electrolyte solutions. The model of Lencka et al. has been shown to reproduce experimental data for concentrations up to $30\,mol\,kg^{-1}$ and temperatures up to $300\,°C$.

In mixed-solvent electrolyte solutions, viscosity is affected not only by the concentration of electrolytes, but also by the composition of the solvent. Even the viscosity of solvent mixtures may show a complex behavior and change significantly with composition. In addition, in systems with strong ion association effect (e.g., in fully miscible acids or bases), viscosity is affected by concentrations of both ions and associated ion pairs. Thus, a comprehensive treatment of viscosity of mixed-solvent electrolyte systems requires taking into account not only the ion–solvent and ion–ion interactions that predominate in aqueous solutions, but also the solvent–solvent and ion pair–solvent interactions.

The objective of this work is to develop a comprehensive, engineering-oriented model for predicting viscosities of mixed-solvent electrolyte solutions. The model is designed to be applicable to mixed-solvent electrolyte solutions over wide ranges of solvent composition and electrolyte concentration (i.e., from infinitely dilute to concentrated salt solutions). Further, it should account for speciation effects, such as complexation or ion association, when combined with a speciation-based thermodynamic model. The model developed in this study consists of two parts: (1) computation of viscosities of pure and mixed solvents as functions of temperature and solvent composition and (2) computation of the dependence of viscosity on electrolyte concentration.

2. Viscosities of solvent mixtures

It has long been recognized that viscosity versus composition curves are not a simple function of composition. They may have a maximum, a minimum or both. Various models for representing the viscosity of a liquid mixture have been described in the literature. Some notable models include those based on the absolute reaction rate theory of Eyring [5] such as the model of McAllister [6] and its various extensions

[7–9]; models based on group contribution methods such as of those of Isdale et al. [10], Cao et al. [11] and Wu [12]; models based on the corresponding-states principle such as those of Teja and Rice [13] and Wu and Asfour [14]; and other empirical approaches such as the models of Giro et al. [15] and Grunberg and Nissan [16]. Although these models have been shown to be capable of representing viscosities of a number of binary and some ternary mixtures, insufficiently accurate results can often be obtained for some specific systems, especially those with polar components such as aqueous mixtures [17]. For example, the Teja–Rice equation showed an average deviation of 9.3% for aqueous systems with a maximum deviation of 44.3% for the water–2-propanol mixture. Such deviations are substantially higher than those for other types of mixtures [13]. In addition, the Teja–Rice model shows a strong dependence of the calculated results on the selection of reference liquids [14]. Similarly, both the Grunberg–Nissan [16] and McAllister [6] equations show large deviations when applied to aqueous systems. Various modifications of the McAllister equation [7–9] significantly reduce the deviations by introducing additional parameters. In the case of ternary mixtures, ternary interaction parameters are introduced in these models [7–9], which limits their predictive capabilities.

In this section, we develop a new mixing rule that relates the viscosities of solvent mixtures to those of pure components. Here, emphasis is put on the accurate representation of the complex composition dependence of viscosity, which is frequently observed in aqueous systems. No attempt is made to predict the viscosities of pure components since this is the domain of group contribution methods. Rather, we utilize empirical correlations for the viscosity of pure components as a function of temperature [18,19] and develop a mixing rule to capture the composition dependence of the viscosity of mixtures. This mixing rule will provide a basis for the computation of viscosities in mixed-solvent electrolyte solutions.

The new mixing rule relates the viscosity of a solvent mixture η_{mix} to pure component viscosities using modified volume fractions, i.e.,

$$\eta_{mix} = \sum_i \sum_j Y_i Y_j \eta_{ij} \tag{2}$$

where Y_i is a modified volume fraction of component *i*:

$$Y_i = \frac{v_i^* x_i}{\sum_k v_k^* x_k} \tag{3}$$

In Eq. (3), the effective volume v_i^* is related to the actual volume v_i^0 by

$$v_i^* = v_i^0 + \sum_{k \neq i} x_k^{1/4} v_k^0 g_{ik} \tag{4}$$

The parameter η_{ij} in Eq. (2) is a modified arithmetic average of pure component viscosities:

$$\eta_{ij} = \frac{1}{2}(\eta_i^0 + \eta_j^0)(1 + k_{ij}) \tag{5}$$

In Eqs. (2)–(5), x_i is the mole fraction of component i, and v_i^0 and η_i^0 are the liquid molar volume and viscosity of component i, respectively. The values of v_i^0 and η_i^0 are available from the compilations of Barthel et al. [18] and Daubert and Danner [19]. Finally, g_{ij} and k_{ij} are the binary parameters for components i and j, which can be determined from experimental viscosity data for mixtures. The g_{ij} parameter accounts for the effect of asymmetry of molar volumes on the variation of the viscosity with composition. It has been found that the symmetry of the viscosity versus composition curve (including the location of a possible maximum or minimum) strongly depends on the modified molar volumes v_i^* (cf. Eq. (3)). The formula for v_i^* has been found empirically on the basis of its effectiveness for representing experimental data. Eq. (4) with x raised to the 1/4 power has been found to give the best accuracy. The quantity v_i^* may be interpreted as an effective molar volume of a component, which is affected by the presence of other components in the mixture. This effect can be represented by Eq. (4) where the pure liquid molar volume (v_i^0) is corrected for the presence of other components, k ($k \neq i$). It should be noted that, when $g_{ik} = 0$ for all i and k, v_i^* reduces to v_i^0 and when all $k_{ij} = 0$, Eq. (2) becomes a volume fraction-averaged simple mixing equation.

3. Dependence of viscosity on electrolyte concentration

In the model of Lencka et al. [4], the dependence of the viscosity on electrolyte concentration is represented by three contributions, i.e., (1) the long-range electrostatic term (η_r^{LR}), which accounts for the interactions between point charges in a dielectric continuum and is calculated based on the Onsager–Fuoss theory [20]; (2) the contribution of individual ions (η_r^s), which is characterized by the viscosity B coefficients; and (3) the contribution of interactions between ions or neutral species (η_r^{s-s}). The general methodology used in the model of Lencka et al. is applicable to electrolyte solutions in any single solvent. To extend this methodology to mixed-solvent electrolyte systems, it is necessary to take into account of the effects of changing solvent composition on the contributions of individual ions and on the interactions between species. An extension of the approach of Lencka et al. to mixed-solvent electrolytes is developed in this section. In this study, the term "mixed-solvent electrolytes" is used in the broadest possible sense to include (1) electrolytes in pure organic or mixed organic-water solvents, (2) fully miscible acids or bases in water, and (3) aqueous electrolyte solutions from the dilute region to the molten salt limit.

For the analysis of the viscosity of aqueous solutions, expressions for the relative viscosity, η_r, are commonly used to represent the effect of electrolyte concentrations. In mixed-solvent electrolyte solutions, due to the combined effects of electrolyte concentration and solvent composition, the relative viscosity is no longer an obvious measure of the electrolyte effect. Analysis of experimental viscosity data of such
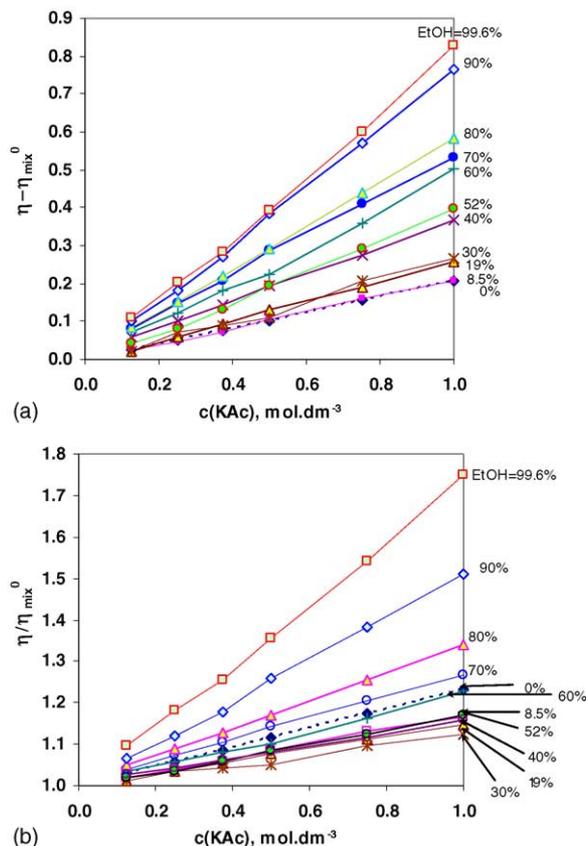

Fig. 1. Variations of (a) $\eta - \eta_{mix}^0$ and (b) η/η_{mix}^0 with the electrolyte concentration at various solvent compositions in the ternary system potassium acetate + ethanol + H$_2$O. The experimental data are from Padova [34]. The lines connecting the data points are shown only for illustrating experimental trends and do not represent modeling results.

systems has revealed that the difference between the viscosity of the solution (η) and that of the solvent mixture (η_{mix}^0) shows relatively simple regularities as a function of both the electrolyte concentrations and solvent composition. On the other hand, no such regularities can be observed for the relative viscosity. This behavior is illustrated in Figs. 1 and 2 for the system potassium acetate + ethanol + water. In Fig. 1a and b, the quantities $\eta - \eta_{mix}^0$ and η/η_{mix}^0, respectively, are plotted as a function of potassium acetate concentration at various solvent compositions. In Fig. 2, these quantities are plotted with respect to the mole fraction of ethanol in the solvent. These figures illustrate that the relative viscosity does not show a simple, regular behavior with respect to solvent composition as the electrolyte concentration varies (Fig. 1b). Instead, it shows a complex behavior with a minimum as a function of solvent composition at each electrolyte concentration. On the other hand, $\eta - \eta_{mix}^0$ shows regular and monotonic variations with respect to both electrolyte and solvent concentrations. Thus, the $\eta - \eta_{mix}^0$ difference appears to be most convenient as the primary quantity for which the model is defined. Following the previous study of Lencka et al. [4], we express the $\eta - \eta_{mix}^0$ difference as a sum of a long-range electrostatic interaction term, contributions of individual species and those
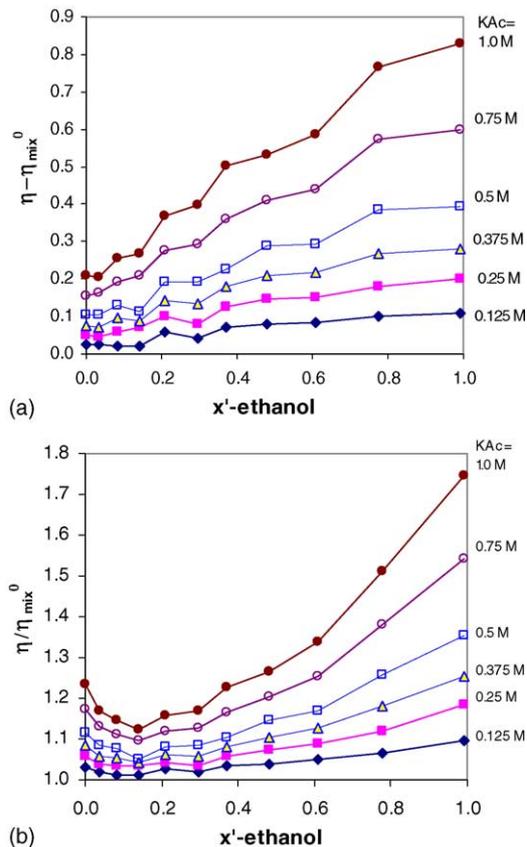
Fig. 2. Variations of (a) $\eta - \eta_{mix}^0$ and (b) η/η_{mix}^0 with the solvent compositions at various electrolyte concentrations in the ternary system potassium acetate + ethanol + H$_2$O. The experimental data are from Padova [34]. The lines connecting the data points are shown only for illustrating experimental trends and do not represent modeling results.

of species–species interactions:

$$\eta - \eta_{mix}^0 = \Delta\eta^{LR} + \Delta\eta^s + \Delta\eta^{s-s} \tag{6}$$

The $\Delta\eta^s$ and $\Delta\eta^{s-s}$ terms are reformulated in this study to account for solvent effects. The long-range electrostatic contribution to the relative viscosity of the electrolyte solution, $\Delta\eta^{LR}$, is calculated using the analytical model developed by Onsager and Fuoss [20]. Expressions for the calculation of $\Delta\eta^{LR}$ are summarized in the Appendix A. The dielectric constant and limiting conductivities of ions, which are used to calculate $\Delta\eta^{LR}$, pertain to those of solvent mixtures. These parameters are calculated using the general models described in previous papers [21,22].

The contribution of individual ions $\Delta\eta^s$ is represented in terms of the viscosity B coefficients. In a solution with a single solvent, this term is rigorously expressed as a simple sum of ionic contributions, i.e.,

$$\Delta\eta^s = \sum_i \eta^0 c_i B_i \tag{7a}$$

where the subscript i denotes all solute species and η^0 is the viscosity of the pure solvent. For mixed-solvent systems, Eq. (7a) is generalized by taking into account that the B coef-

ficients are solvent-dependent and η^0 is no longer a single quantity, but is replaced by those for multiple solvents. Thus, Eq. (7a) is rewritten for multiple solvents as:

$$\Delta\eta^s = \sum_j \sum_i x_j \eta_j^0 c_i B_{i,j} \tag{7b}$$

where the subscript j denotes the solvent components, i pertains to the solutes (ions and neutral species); η_j^0 is the viscosity of pure solvent j; c_i is the molarity (mol L^{-1}) of the ith species, $B_{i,j}$ is the B coefficient of the ith species in a pure solvent j and x_j is the mole fraction of solvent j on a salt-free basis.

In a previous paper, Lencka et al. [4] developed an expression for η_r^{s-s} that is valid for multi-component solutions in a single solvent. This term is proportional to I^2 (where I is the ionic strength of the solution) and is made up of contributions of all species pairs in the system, i.e.,

$$\Delta\eta^{s-s} = \sum_i \sum_j \eta^0 f_i f_j D_{ij} I^2 \tag{8a}$$

where f_i and f_j are fractions of the ith and jth species, respectively, and D_{ij} is the interaction parameter between i and j. In this study, we generalize this expression to recognize that the effects of species–species interactions are dependent on the solvent combinations. The multi-solvent extension of Eq. (8a) is given by

$$\Delta\eta^{s-s} = \sum_j \sum_l \sum_i \sum_k x_j x_l \eta_{jl}^0 f_i f_k D_{ik,jl} I^2 \tag{8b}$$

where the first and second sums (j and l) are over all solvents and the sums over i and k are over all solutes; η_{jl}^0 is an averaged viscosity of solvents j and l,

$$\eta_{jl}^0 = \frac{1}{2}(\eta_j^0 + \eta_l^0) \tag{9}$$

As in the single-solvent model [4], the fractions f_i and f_k are molar fractions of the ith and kth species, respectively, adjusted for the charges of species, i.e.,

$$f_i = \frac{c_i/\max(1, |z_i|)}{\sum_l c_l/\max(1, |z_l|)} \tag{10}$$

where the factor $\max(1,|z_i|)$ ensures that f_i reduces to the molar fraction for neutral species. $D_{ik,jl}$ is a binary parameter between the species i and k in a solvent pair j and l, and I is the ionic strength extended to include the molarities of ion pairs (as opposed to solvent molecules), which typically become predominant at high concentrations because of speciation equilibria, i.e.,

$$I = \sum_{\text{ions}} z_i^2 c_i + \sum_{\text{ion-pair}} c_n \tag{11}$$

The molar concentrations of all species in the above equations are calculated using speciation and density obtained from a recently developed thermodynamic model [23]. It should be noted that, in cases when there is only one solvent, the

new model reduces to that of Lencka et al. [4] for aqueous electrolyte solutions.

4. Parameter evaluation

4.1. Mixing rule parameters g_{ij} and k_{ij}

Based on Eqs. (2)–(5), the viscosity of a solvent mixture can be calculated using viscosities and densities of pure solvent components. The variation of these properties with temperature frequently provides sufficient temperature dependence for the viscosity of mixtures. In such cases, no additional temperature dependence needs to be introduced for the g_{ij} and k_{ij} parameters. However, when experimental data cover a wide range of temperatures, the accuracy of calculating the viscosity of solvent mixtures can be improved if the mixing rule parameters are expressed as

$$g_{ij} = g_{ij}^{(0)} + \frac{g_{ij}^{(1)}}{T} \tag{12a}$$

and

$$k_{ij} = k_{ij}^{(0)} + \frac{k_{ij}^{(1)}}{T} \tag{12b}$$

4.2. The B coefficients

The B coefficients for a large number of aqueous species have been determined by analyzing extensive experimental viscosity data [4]. Marcus [24] has compiled the B coefficients for a number of ions in pure organic solvents at 25 °C. For the systems for which the B coefficients are not available in literature sources, their values have been deter-mined from experimental viscosity data at low electrolyte concentrations (usually below 0.05 M) in pure solvents using a method described by Lencka et al. [4]. The extensive compilation of Barthel et al. [18], which reports experimental results for the viscosity of electrolytes in alcohol solutions and in other protic and aprotic solvents, was used as a source of data for the determination of the B coefficients in organic solvents. Frequently, experimental viscosity data for non-aqueous electrolytes are reported only at much higher concentrations, making it difficult to determine the B coefficients. In such cases, the B parameters have been treated as adjustable constants, together with the interaction parameters $D_{ik,jl}$, and have been determined using viscosity data for binary electrolyte + solvent system.

The temperature dependence of the B coefficients is expressed using the equation of Out and Los [25]:

$$B = B_E + B_S \exp(-K(T - T_0)) \tag{13}$$

where T is the temperature in K, $T_0 = 273.15$ K, and K has been set equal to 0.023 for most aqueous [4] and non-aqueous electrolyte solutions. In some cases, K can also be treated as an adjustable parameter, together with B_E and B_S. Since the B coefficient is a characteristic parameter for ions, and is a manifestation of effects such as ion solvation and structure breaking or structure making, various correlations have been developed between the B coefficient and ion properties such as the partial molal entropy [26], molar volume of hydrated salts [27], and standard entropy of hydration [4,28]. Such correlations make it possible to predict the B coefficients using easily available information. However, these correlations have been developed only for aqueous electrolyte solutions. Development of similar correlations for mixed-solvent systems can be expected to be more challenging due to the lack

Table 1
Parameters of Eqs. (4) and (5) for selected solvent pairs

Solvent pairs		Parameters		T, (°C)	Relevant systems	Number of points	AAD	References
i	j	$k_{ij}^{(0)}\ g_{ij}^{(0)}$	$k_{ij}^{(1)}\ g_{ij}^{(1)}$					
Methanol	H$_2$O	−7.8686	3030.6	10–50	Methanol–water	41	3.29	[8,9]
		1.40337	−434.837		Methanol–ethanol–water	69	5.83	
					Methanol–acetone–water	28	3.52	
Methanol	Acetone	−0.1750	0.0	25–30	Methanol–acetone	15	2.11	[8,9]
		0.0	0.0		Methanol–acetone–water	28	3.52	
Acetone	H$_2$O	−5.655	2415.0	20–50	Acetone–water	55	6.33	[8,9]
		−0.09	0.0		Methanol–acetone–water	28	3.52	
Ethanol	H$_2$O	−16.927	5854.36	10–50	Ethanol–water	91	9.40	[9,33]
		1.62221	−469.835		Methanol–ethanol–water	69	5.83	
Methanol	Ethanol	0.951926	−342.158	10–50	Methanol–ethanol	63	0.96	[9]
		0.00.0	0.0		Methanol–ethanol–water	69	5.83	
					Methanol–ethanol–propanol	24	3.12	
Propanol	Methanol	−0.396836	0.0	30	Propnanol–methanol	14	3.75	[9]
		0.407171	0.0		Methanol–ethanol–propanol	24	3.12	
Propanol	Ethanol	−0.103246	0.0	30	Propnanol–ethanol	12	0.75	[9]
		0.151893	0.0		Methanol–ethanol–propanol	24	3.12	

of appropriate ion property data in solvents other than water. Such correlations are outside the scope of this study.

4.3. The $D_{ik,jl}$ parameters

The temperature and ionic strength dependence of the $D_{ik,jl}$ parameters was introduced by Lencka et al. [4] and remains unchanged in the present work. The general expression for $D_{ik,jl}$ is

$$D_{ik,jl} = d_{ik,jl}^{(1)} + d_{ik,jl}^{(2)}I + d_{ik,jl}^{(3)}\exp(bI^{3/2}) \qquad (14)$$

where b is set equal to 0.08 for most aqueous and non-aqueous electrolyte solutions, but may be treated as an adjustable parameter if necessary. The temperature dependence of each of the $d_{ik,jl}^{(m)}$ ($m = 1, 2, 3$) parameters is given by

$$d_{ik,jl}^{(m)} = d_{ik,jl}^{(m0)}\exp(d_{ik,jl}^{(m1)}(T - T_0)), \quad (m = 1, 2, 3) \qquad (15)$$

5. Results and discussion

5.1. Viscosities of solvent mixtures

Viscosity data for a number of binary and ternary solvent mixtures have been used for validating the correlation described in Section 2. Table 1 lists the parameters g_{ij} and k_{ij} (Eqs. (2)–(5)) for selected systems, together with the average percentage error, which is defined by

$$\text{AAD} = \frac{\sum_k 100|\eta_{\text{exp}} - \eta_{\text{cal}}|/\eta_{\text{exp}}}{m} \qquad (16)$$

where m is the number of experimental data points. Results for selected binary systems are shown in Figs. 3–5. To validate the model against ternary or higher-order systems, the mixing rule parameters obtained from binary data were used to predict the viscosity of ternary systems. The results are shown in
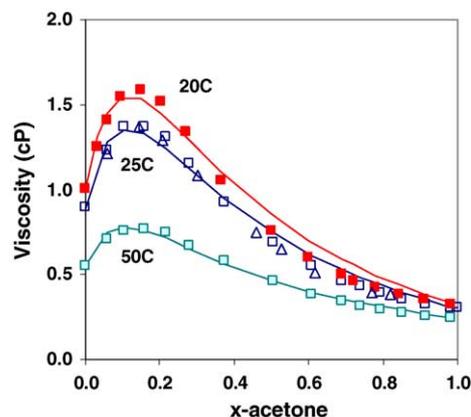
Fig. 3. Viscosity of acetone + water mixtures as a function of the acetone mole fraction at 20, 25, and 50 °C. Experimental data were taken from Noda et al. [8] ($\triangle$) and Dizechi and Marschall [9] (($\square$) and ($\blacksquare$)). The lines are calculated using Eqs. (2)–(5).

Fig. 6 in the form of relative deviations of the calculated viscosities for four ternary mixtures containing methanol. The results shown in these figures and in Table 1 indicate that the mixing rule (Eqs. (2)–(5)) can accurately reproduce experimental data for liquid mixtures of any composition.

5.2. Viscosities of mixed-solvent electrolyte solutions

As discussed above, the viscosity model of Lencka et al. [4] has been shown to be accurate for aqueous electrolyte solutions with concentrations up to 30 mol kg^{-1}. The new viscosity model (Eqs. (6)–(8)) reduces to the model of Lencka et al. [4] when water is the only solvent in the system. Thus, validation of the new viscosity model has been focused on the following systems: (1) electrolytes in pure organic and mixed solvents and (2) aqueous electrolyte solutions (salts, acids, and bases) ranging from the dilute region to fused salts or pure acids or bases. Experimental viscosity data for such
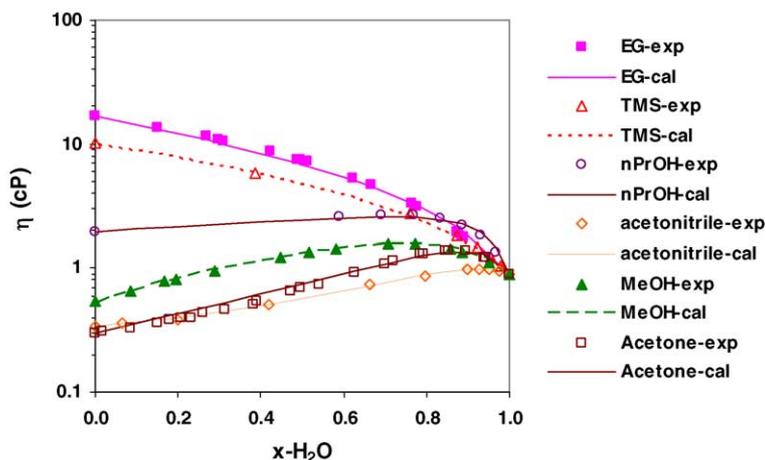

Fig. 4. Viscosity of organic-water mixtures as a function of the mole fraction of water at 25 °C. Experimental data were taken from Sesta and Berardelli [35] (ethylene glycol), D'Aprano et al. [36] (tetramethylene sulfone (TMS)), Niazi et al. [37] (n-propanol), Singh et al. [38] and Petrella et al. [39] (acetonitrile), Noda et al. [8] (methanol and acetone), and Dizechi and Marschall [9] (acetone). The lines are calculated using Eqs. (2)–(5).
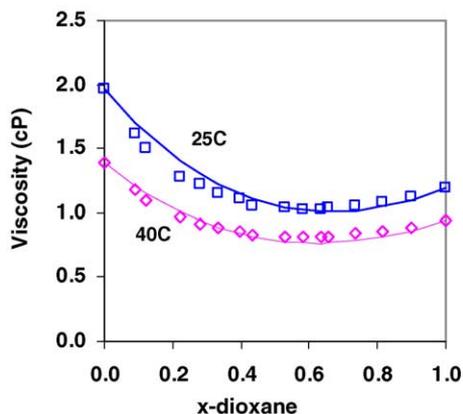
Fig. 5. Viscosity of dioxane + n-propanol mixtures at 25 and 40 °C as a function of the mole fraction of dioxane. Experimental data were taken from Contreras [40]. The lines are calculated using Eqs. (2)–(5).
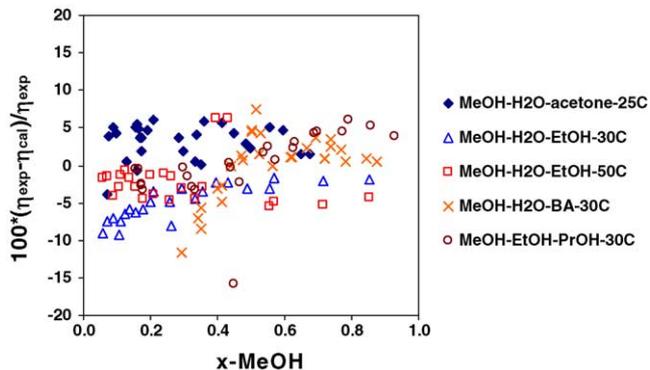

Fig. 6. Percentage deviations for the prediction of viscosities as a function of x_{methanol} for ternary systems containing methanol. Experimental data were taken from Dizechi and Marschall [9] (methanol + ethanol + water and methanol + ethanol + propanol), Noda et al. [8] (methanol + acetone + water), and Visak et al. [41] (methanol + butyl acetate + water). The calculated viscosities are obtained from Eqs. (2)–(5) using parameters obtained by regressing data for only the constituent binary subsystems.

systems are available in extensive compilations [18,28,29] and in other literature sources. For all of the systems for which the viscosity model has been tested, thermodynamic model parameters [23] were first developed to provide accurate speciation and density input to viscosity modeling.

Table 2 shows the adjustable parameters in Eqs. (8), (14) and (15) for selected aqueous and mixed-solvent electrolyte systems. The performance of the model for electrolytes in pure organic and mixed solvents is shown in Figs. 7–10. In these figures, experimental viscosity data for the sys-

tems $LiNO_3$ + ethanol + water, Na acetate + acetone + water, K acetate + ethanol + H_2O, $CaCl_2$ + methanol + H_2O, and $SbCl_3$ + methanol are compared with calculated results at various solvent compositions, electrolyte concentrations, and temperatures. The average percentage deviations, AAD, as defined by Eq. (16), are given in the figures captions.

Table 2
Parameters of Eqs.) for selected systems

System and conditions[a]	Parameters	
H_2SO_4 + water; $T = 0–100$ °C; $x_{H_2SO_4} = 0–1$	$d^{(10)}_{H^+,HSO_4^-/H_2O,H_2O} = -0.91626$	$d^{(10)}_{H^+,HSO_4^-/H_2SO_4,H_2SO_4} = 0.246094$
	$d^{(20)}_{H^+,HSO_4^-/H_2O,H_2O} = 0.13489E-01$	$d^{(20)}_{H^+,HSO_4^-/H_2SO_4,H_2SO_4} = -0.182758E-01$
	$d^{(30)}_{H^+,HSO_4^-/H_2O,H_2O} = 0.73300$	$d^{(30)}_{H^+,HSO_4^-/H_2SO_4,H_2SO_4} = 0.673728E-04$
	$d^{(11)}_{H^+,HSO_4^-/H_2O,H_2O} = -0.30684E-01$	$d^{(11)}_{H^+,HSO_4^-/H_2SO_4,H_2SO_4} = -0.925755E-02$
	$d^{(21)}_{H^+,HSO_4^-/H_2O,H_2O} = -0.61230E-01$	$d^{(21)}_{H^+,HSO_4^-/H_2SO_4,H_2SO_4} = -0.578415E-02$
	$d^{(31)}_{H^+,HSO_4^-/H_2O,H_2O} = -0.18162E-01$	$d^{(31)}_{H^+,HSO_4^-/H_2SO_4,H_2SO_4} = 0.797305E-02$
	$b = 0.69679E-02$	$b = 0.08$
$LiNO_3$ + water; $T = 0–130$ °C; $m_{LiNO_3} = 0–40$ mol kg^{-1}	$d^{(10)}_{Li^+,NO_3^-/H_2O,H_2O} = -0.493160E-01$	$d^{(10)}_{Li^+,NO_3^-/H_2O,ethanol} = -0.602772$
	$d^{(20)}_{Li^+,NO_3^-/H_2O,H_2O} = 0.214070E-07$	$d^{(20)}_{Li^+,NO_3^-/H_2O,ethanol} = 0.101641$
	$d^{(30)}_{Li^+,NO_3^-/H_2O,H_2O} = 0.767688E-01$	$d^{(30)}_{Li^+,NO_3^-/H_2O,ethanol} = 0$
		$b = 0.08$
$LiNO_3$ + water + ethanol[b]; $T = 25$ °C; $x_{ethanol} = 0–1$; $m_{LiNO_3} = 0–24$ mol kg^{-1}	$d^{(11)}_{Li^+,NO_3^-/H_2O,H_2O} = -0.495330E-01$	$d^{(10)}_{Li^+,NO_3^-/ethanol,ethanol} = 0.118950$
	$d^{(21)}_{Li^+,NO_3^-/H_2O,H_2O} = 0.789590E-01$	$d^{(20)}_{Li^+,NO_3^-/ethanol,ethanol} = 0.489974$
	$d^{(31)}_{Li^+,NO_3^-/H_2O,H_2O} = -0.133438E-01$	$d^{(30)}_{Li^+,NO_3^-/ethanol,ethanol} = 0$
	$b = 0.309001E-01$	$b = 0.08$

[a] Experimental viscosity data under these conditions were used to determine the parameters.

[b] $d^{(11)}$, $d^{(21)}$, $d^{(31)}$ for $L_i^+,NO_3^-/H_2O$, ethanol and {Li^+,NO_3^-/ethanol, ethanol} cannot be determined due to the lack of viscosity data at temperatures other than 25 °C. They are set equal to zero.
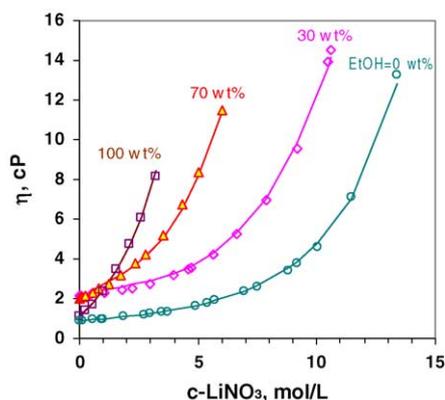
Fig. 7. Viscosities of ternary $LiNO_3$–ethanol–H_2O solutions as a function of the molarity of $LiNO_3$ for various solvent compositions at 25 °C. The experimental data are from Campbell and Debus [42]. The lines have been obtained from the model. The average percentage deviation is 2.20.

As shown in Fig. 7, viscosity increases more rapidly with $LiNO_3$ concentration as the ethanol weight fraction increases in the $LiNO_3$ + ethanol + H_2O system. This trend is also predicted for the $CaCl_2$ + methanol + H_2O system as shown in

Fig. 9b. Upon addition of a salt, the qualitative trends in the composition dependence of viscosity in salt + solvent mixtures remain similar to those in salt-free solvent mixtures. In the case of the Na acetate + acetone + H_2O and K acetate + ethanol + H_2O systems, the viscosities show a maximum with changing solvent composition at all salt concentrations (cf. Fig. 8). These trends are accurately reproduced by the model.

Metal nitrates in water can be continuously miscible from infinite dilution to the fused salt limit. Since extensive experimental viscosity data are available for such systems [30,31], they provide a stringent test of the performance of the model over the full concentration range of electrolyte components. Fig. 11 shows the results for the ternary system $AgNO_3$–$TlNO_3$–water at water contents ranging from $x_w = 0$ to 0.98 and at a constant Ag/Tl molar ratio of 1.06, which corresponds to a eutectic mixture of $AgNO_3$ and $TlNO_3$. The calculated and experimental results are in excellent agreement.

Fully miscible aqueous acids and bases are another important class of mixtures. Because of their usually strong
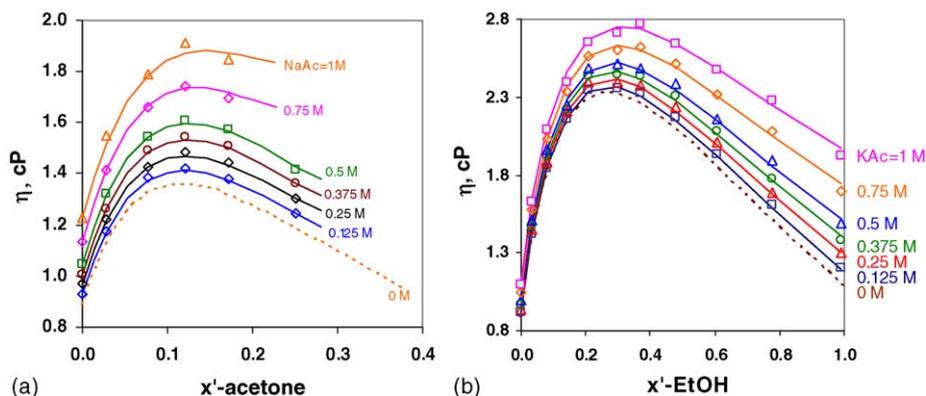

Fig. 8. Viscosities of the ternary systems (a) sodium acetate + acetone + H_2O and (b) potassium acetate + ethanol + H_2O at 25 °C as a function of the mole fraction of the organic solvent (on a salt-free basis) for various salt molarities. The dashed lines represent the viscosity of solvent mixtures. The experimental data are from Padova [34]. The lines have been obtained from the model. The average percentage deviations are 0.48 in the case of (a) and 0.84 in (b).
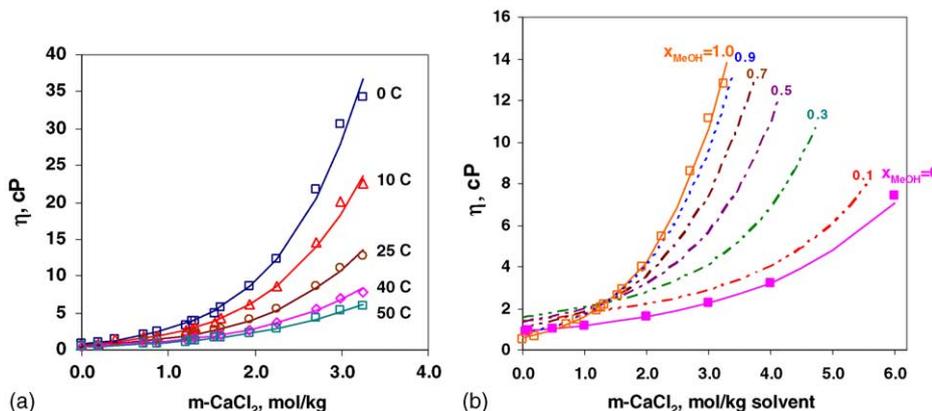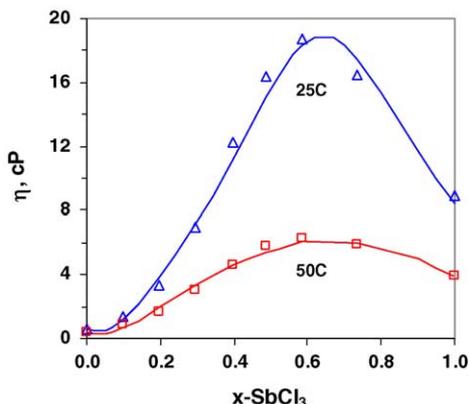

Fig. 9. Viscosities of (a) $CaCl_2$ + methanol solutions as a function of the molality of $CaCl_2$ at various temperatures and (b) $CaCl_2$ + methanol + water solutions as a function of the molality of $CaCl_2$ at various methanol mole fractions at 25 °C. The experimental data in pure methanol are from Wahab and Mahiuddin [43] and those in water are from Lobo [29]. The lines are calculated using the model. The results for the mixture of methanol + water ($x_{methanol} \neq 0$ and 1, dashed lines) were predicted. The average percentage deviation in the fit for $CaCl_2$ + methanol viscosities is 3.33.

Fig. 10. Viscosities of SbCl$_3$–methanol solutions as a function of the mole fraction of SbCl$_3$ at 25 and 50 °C. The experimental data are from Fialkov and Basov [44]. The lines are calculated from the model. The average percentage deviation is 7.38.
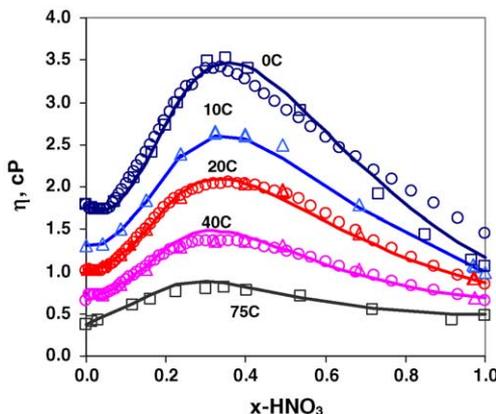

Fig. 12. Viscosities of HNO$_3$–water solutions as a function of the mole fraction of HNO$_3$ at various temperatures. Experimental data are from Bingham and Stone [45] (($\triangle$) at 10, 20, and 40 °C), Rhodes and Hodge [46] (($\square$) at 0 °C and 75 °C), and Zaytsev and Aseyev [47] (($\bigcirc$) at 0, 20, and 40 °C). The lines are calculated from the model. The average percentage deviation between the calculated and experimental viscosities is 2.81.

association effects, such systems provide not only good test cases, but also offer an excellent opportunity to examine the effect of speciation on viscosity. When modeling fully miscible acids, both water and the undissociated acid molecules (e.g., H$_2$SO$_4^0$ or HNO$_3^0$) have been treated as solvent components. In these systems, speciation can change dramatically as acid concentration increases. In particular, a significant amount of neutral acid molecules may exist as the acid concentration approaches a mole fraction of unity and the association is nearly complete in a pure acid [32]. The interaction parameters that are used in the model are defined as those between the predominant ions (e.g., H$^+$ and HSO$_4^-$ in the H$_2$SO$_4$ + H$_2$O system or H$^+$ and NO$_3^-$ in HNO$_3$ + H$_2$O) in each of the two solvents or in the solvent mixtures. For example, the best fits were obtained for the H$_2$SO$_4$ + H$_2$O system when the parameters $D_{H^+/HSO_4^-,H_2O/H_2O}$ and $D_{H^+/HSO_4^-,H_2SO_4/H_2SO_4}$ were

introduced. In the HNO$_3$ + H$_2$O system, the corresponding parameters are $D_{H^+/NO_3^-,H_2O/H_2O}$ and $D_{H^+/NO_3^-,HNO_3/H_2O}$. Figs. 12–14 show the results for the HNO$_3$ + H$_2$O, H$_2$SO$_4$ + H$_2$O, and HNO$_3$ + H$_2$SO$_4$ systems, respectively, at various temperatures. Results for the ternary mixture of H$_2$SO$_4$ + HNO$_3$ + H$_2$O at 75 °C are shown in Fig. 15. The parameters that were used for this ternary system and the constituent binary mixture H$_2$SO$_4$ + HNO$_3$ are $D_{H^+/HSO_4^-,HNO_3/H_2SO}$, $D_{H^+/HSO_4^-,HNO_3/HNO_3}$, $D_{H^+/HSO_4^-,H_2O/HNO_3}$, and $D_{NO_3^-/HSO_4^-,HNO_3/HNO_3}$. Excellent agreement between experimental and calculated results has been obtained for all of the tested acids over wide ranges of temperature.

Another example of the effect of speciation on viscosity is provided by the SbCl$_3$–methanol system. It has been
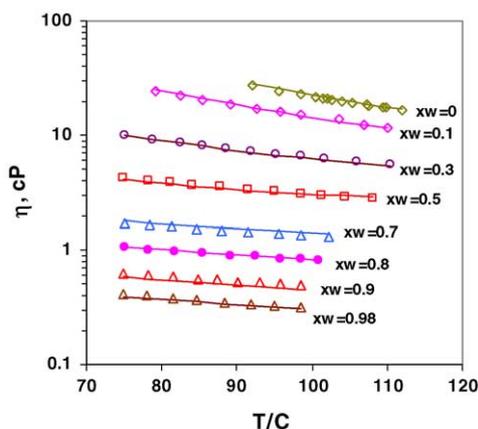

Fig. 11. Viscosities of the ternary system AgNO$_3$–TlNO$_3$–water as a function of temperature at various mole fractions of water (x_w) and at the Ag/Tl molar ratio of 1.06. The lines are calculated using the model and the experimental data are from Abraham and Abraham [30]. The average percentage deviation between the calculated and experimental viscosities is 3.58.
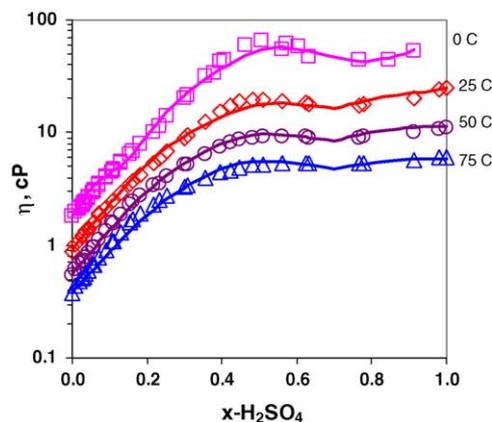

Fig. 13. Viscosities of H$_2$SO$_4$–water solutions as a function of the mole fraction of H$_2$SO$_4$ at various temperatures. The experimental data are from Lobo [29] and Zaytsev and Aseyev [47]. The lines are calculated from the model. The average percentage deviation between the calculated and experimental viscosities is 6.08.
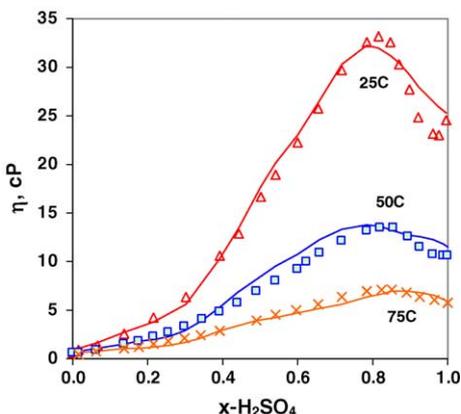
Fig. 14. Viscosities of binary solutions of HNO$_3$ and H$_2$SO$_4$ as a function of the mole fraction of H$_2$SO$_4$ at various temperatures. The experimental data are from Bingham and Stone [45]. The lines are calculated from the model. The average percentage deviation between the calculated and experimental viscosities is 9.43.

Fig. 15. Viscosities of the ternary system HNO$_3$–H$_2$SO$_4$–H$_2$O at 75 °C as a function of water mole fraction at various fixed concentrations of HNO$_3$. The experimental data are from Rhodes and Hodge [46]. The lines are calculated from the model. The average percentage deviation between the calculated and experimental viscosities is 9.24.
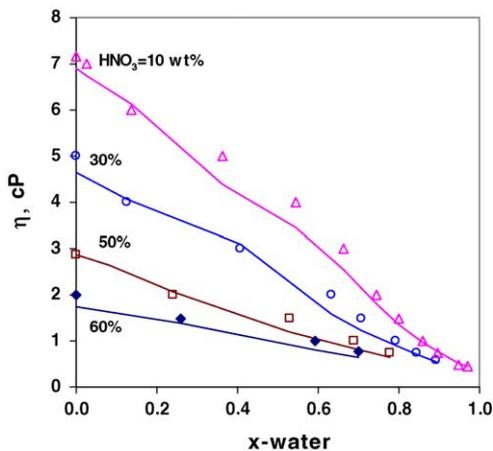
found that the accuracy of viscosity calculations for this system largely depends on the speciation. Specifically, it was necessary to introduce a complex, SbCl$_3{}^0$, to represent the association of Sb^{+3} with Cl$^-$ in methanol. Then, the thermodynamic model was able to yield speciation results that gave an excellent representation of the viscosity data. The results for this system are shown in Fig. 10.

6. Conclusion

A comprehensive model has been developed for calculating the viscosity of concentrated aqueous and mixed-solvent electrolyte solutions. The model consists of two main parts, i.e., a mixing rule for computing the viscosity of solvent mixtures as a function of temperature and solvent composition, and an expression for the effect of finite electrolyte concentrations. The mixing rule utilizes the viscosities and molar volumes of pure components. It has been shown to be very effective for representing experimental data for a variety of solvent mixtures. In particular, the viscosity of ternary solvent mixtures can be accurately predicted using parameters determined only from binary data. To represent the dependence of viscosity on electrolyte concentration, the model includes a long-range electrostatic term ($\Delta\eta^{LR}$) obtained from the Onsager–Fuoss theory, a contribution of individual ions ($\Delta\eta^s$) as quantified by the Jones–Dole B coefficients, and a contribution of specific interactions between ions or neutral species ($\Delta\eta^{s-s}$ New formulations have been developed for both the $\Delta\eta^s$ and $\Delta\eta^{s-s}$ terms to account for the effects of multiple solvents. The viscosity model has been coupled with a thermodynamic equilibrium model [23] to provide speciation, which is necessary for viscosity calculations in electrolyte systems. This makes it possible to reproduce the effects of complexation or other reactions in the solution. In all cases in which experimental data are available, the new model has been shown to be accurate for reproducing viscosities over wide ranges of composition with respect to both solvents and electrolytes. The model has been implemented in software for simulating both thermodynamic and transport properties of electrolyte systems.

List of symbols

B_{ij}	B coefficient of i in pure solvent j
c_i	molar concentration of i
$D_{ik,jl}$	interaction parameter between i and k in a binary mixed solvent of j and l
f_i	fractions of the ith species, defined in Eq. (10)
g_{ik}, k_{ik}	mixing rule parameters (Eqs. (4) and (5))
I	ionic strength, defined by Eq. (11)
v_i^0	molar volume of pure liquid i
v_i^*	redefined molar volume of i, see Eq. (4)
x_i	mole fraction of i
Y_i	modified volume fraction of i, defined in Eq. (3)
η	viscosity of the solution
η_{mix}, η_{mix}^0	viscosity of the solvent mixture
η_i^0	viscosity of pure liquid i
η_{ij}	modified arithmetic average of viscosities of i and j, defined by Eq. (5)

Appendix A

According to the Onsager–Fuoss theory [20], the long-range electrostatic interaction contribution to viscosity is given by

$$\Delta\eta^{LR} = a\left(\frac{2I}{\varepsilon T}\right)^{1/2}\left[\left(\sum_i^{N_I}\frac{\mu_i z_i}{\lambda_i}\right) - 4\mathbf{r}\sum_{n=0}^{\infty}c_n s^n\right] \quad (A.1)$$

where ε is the dielectric constant of the solvent and a is a numerical constant defined by

$$a = \frac{Fe^2 10^8}{480\pi}\left(\frac{N_A}{1000\varepsilon_0 k_B}\right)^{1/2} = 0.36454 \quad (A.2)$$

where F, e, N_A, ε_0 and k_B are the Faraday constant, electron charge, Avogadro constant, permittivity of vacuum and Boltzmann constant, respectively. The numerical factors in Eq. (A.2) apply when the concentration in expressed in (mol/dm^3) and ionic conductivity in $(\Omega^{-1}\,mol^{-1}\,cm^2)$. I is the ionic strength in (mol/dm^3). In Eq. (A.1), N_I is the total number of different ions in the mixture, z_i is the absolute value of the ionic charge, λ_i is the equivalent conductance of ion i and μ_i is defined as

$$\mu_i = \frac{c_i z_i^2}{\sum_j^{N_I} c_j z_j^2} \quad (A.3)$$

The vector $\mathbf{r}$ is given by

$$r_i = 1 - \frac{z_i/\lambda_i}{\overline{(z/\lambda)}}, \quad i = 1, \ldots, N_I \quad (A.4)$$

where the average $\overline{(z/\lambda)}$ is calculated as

$$\overline{(z/\lambda)} = \frac{\sum_i^{N_I} c_i z_i^2 (z_i/\lambda_i)}{\sum_i^{N_I} c_i z_i^2} \quad (A.5)$$

In Eq. (A.1), c_n is a numerical factor defined as

$$c_0 = -3 + \sqrt{2} \quad (A.6)$$

$$c_n = -2\sqrt{2}\left\{\sqrt{2} - \sum_{p=0}^{n}\binom{1/2}{p}\right\}, \quad n = 1, \ldots, \infty \quad (A.7)$$

The vectors $\mathbf{s}^n$ are given by a recursive formula, i.e.,

$$\mathbf{s}^0 = \mathbf{s} \quad (A.8)$$

$$\mathbf{s}^n = \mathbf{H}\mathbf{s}^{n-1} \quad (A.9)$$

where the elements of the vector $\mathbf{s}$ are defined as

$$s_j = \mu_j\left(\frac{z_j}{\lambda_j} - \frac{\overline{(z/\lambda)^2}}{\overline{(z/\lambda)}}\right) \quad (A.10)$$

The second-order average $\overline{(z/\lambda)^2}$ is calculated as

$$\overline{(z/\lambda)^2} = \frac{\sum_i^{N_I} c_i z_i^2 (z_i/\lambda_i)^2}{\sum_i^{N_I} c_i z_i^2} \quad (A.11)$$

The matrix $\mathbf{H}$ in Eq. (A.9) is defined as

$$h_{ji} = 2\delta_{ji}\sum_k^{N_I}\mu_k\frac{\lambda_k/z_k}{\lambda_k/z_k + \lambda_j/z_j} + 2\mu_j\frac{\lambda_j/z_j}{\lambda_i/z_i + \lambda_j/z_j} - \delta_{ji} \quad (A.12)$$

where δ_{ij} is the Kronecker symbol. The second summation in Eq. (A.1) usually reaches convergence for n ranging from 4 to 6.

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